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Utilization of sewage sludge in EU application of old and new methods—A review

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Abstract

The European Union has made progress in dealing with municipal wastewater in individual countries and as a corporate entity. However, it intends to make still further and substantial progress over the next 15 years. Currently, the most widely available options in the EU are the agriculture utilization, the waste disposal sites, the land reclamation and restoration, the incineration and other novel uses. The selection of an option on a local basis reflects local or national, cultural, historical, geographical, legal, political and economic circumstances. The degree of flexibility varies from country to country. In any case sludge treatment and disposal should always be considered as an integral part of treatment of wastewater. There is a wide range of other uses for sludge, which exploit its energy or chemical content, namely the thermal processes. The present paper sought to review past and future trends in sludge handling, focusing mainly at thermal processes (e.g. pyrolysis, wet oxidation, gasification) and the utilization of sewage sludge in cement manufacture as a co-fuel.

Keywords: Sewage sludge; Handling methods; Thermal methods; Mortars; Fuel

Contents

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1. Introduction

It is widely accepted that interest in environmental issues is constantly increasing. At the same time, environmental issues have gradually been broadened with concepts, such as sustainable development, which implies not only ecological, but also economic and social responsibilities. The handling of sewage sludge is one of the most significant challenges in wastewater management.

Sewage sludge is regarded as the residue produced by the wastewater treatment process, during which liquids and solids are being separated. Liquids are being discharged to aqueous environment while solids are removed for further treatment and final disposal. The constituents removed during wastewater treatment include grit, screenings and sludge [1]. Of the constituents removed by effluent treatment, sludge is by far the largest in volume, therefore its handling methods and disposal techniques are a matter of great concern. Without a reliable disposal method for the sludge the actual concept of water protection will fail. *Sustainable sludge handling may be defined as a method that meets requirements of efficient recycling of resources without supply of harmful substances to humans or the environment* [2].

The sludge stemming from the wastewater treatment process is usually liquid or semisolid liquid; the concentration which contains 0.25–12% solids by weight [1]. The solid fraction varies between the above limits due to the different methods of the effluent treatment. In Europe, dry weight per capita production of sewage sludge resulting from primary, secondary and even tertiary treatment is in average 90 g per person per day [3]. Additional to the above, the implementation of the Urban Waste Water Treatment Directive (UWWTD) (91/271/EEC) leads to 50% increase in sludge production by year

2005, i.e. 10 million tons annually [2]. The above Directive was introduced in order to improve the aqueous environment, through treating municipal wastewater before releasing it. At the same time, it eliminates the possible adverse effects where such discharges occur. The basic idea of the Directive is to encourage all cities above 2000 PE to implement secondary wastewater treatment. The aforementioned arguments lead to the conclusion that there will be significant increase in sludge production. This is the main drawback, which takes further the issue of sludge handling.

The amount of sludge produced is affected in a limited scale by the treatment efficiency while the sludge quality is strongly dependent on the original pollution load of the treated effluent and also, on the technical and design features of the waste water treatment process.

2. EU legislation concerning sewage sludge

A number of directives on waste treatment have been approved by the European Union, as follows:

- As early as 1975, the waste framework directive required Member States to manage waste by encouraging prevention and environmentally friendly disposal [4].
- The Sewage Sludge Directive 86/278/EEC seeks to encourage the use of sewage sludge in agriculture. At the same time it regulates its use in such a way that any potential harmful effect on soil, vegetation, animals and human beings is prevented. According to the above principle, the use of untreated sludge in agriculture is prohibited, unless it is injected or incorporated in the soil [5]. Moreover, by the term treated sludge is defined the sewage sludge which "has undergone biological, chemical or heat term, long-term storage or any other appropriate process so as significantly to reduce its ferment ability and the health hazards resulting from its use" [6].
- The hazardous waste directive in 1991 set the rules for handling this type of waste [4].
- The Urban Waste Water Directive 91/271/EEC was amended by 98/15/EC is coming into force by year 2005 and sets more stringent quality standards for waste waters. The main article of the Urban Waste Water Treatment Directive dealing with sludge is Article 14, where it is declared that "*sludge arising from waste water treatment shall be re-used whenever appropriate*". In addition, Article 14 also obliges Member States to "*ensure that by 31 December 1998 the disposal of sludge to surface waters by dumping from ships, by discharge from pipelines or by other means is phased out*" [2].
- The European Union set a target of reducing dioxins by 90% between 1985 and 2000. A new directive approved in 2000, which comes into force in 2005, limits the dioxins emitted during incineration.

The European Union's target to reduce final waste disposal by 20% compared with 2000 by 2010 and by 50% by 2050 [7]. To do this, it has drawn up a strategy setting the following priorities: (a) prevention of waste; (b) waste recovery through, reuse, recycling and energy recovery; (c) improved treatment conditions; (d) regulation of transport. Finally, the following European directives are fulfilled through a successful implementation of gasification as a way of power production:

- Legislation concerning emission limits for individual plants/processes (and also fuel quality standards limiting the content of certain compounds in fuel).

- Emissions limits or ceilings at a national level.
- Legislation for local air quality concentration limits (often concerning local plant or processes).
- National or European air quality concentration limits, mandating threshold levels to be met at ambient background areas (objectives or standards).
- National economic instruments (energy or pollution taxes and charges).

3. Sludge characteristics

Sludge, originating from the treatment process of waste water, is the residue generated during the primary (physical and/or chemical), the secondary (biological) and the tertiary (additional to secondary, often nutrient removal) treatment. The sources of solids in a treatment plant vary according to the type of plant and its method operation. Obviously, in order to treat and dispose of the sludge that is produced in a wastewater plant effectively, it is crucial to know the characteristics of the sludge that will be processed. A typical chemical composition and properties of untreated and digested sludge is reported in Table 1 [1]. It should be stated that many of the chemical constituents, including nutrients, are important when considering the ultimate disposal of the processed sludge and the liquid removed from the sludge during treatment. According to Metcalf and Eddy [1] the control of pH levels, alkalinity and organic acid content is an important parameter in the process of anaerobic digestion. Additionally, the content of heavy metals, pesticides and hydrocarbons needs also to be determined when sewage sludge is to be incinerated or land filled. Lastly, the energy (thermal) content of sludge is significant when thermal processes (gasification, pyrolysis, combustion, wet oxidation) are considered [8].

Table 1
Typical chemical composition and properties of untreated/digested sludge

Item/sludge	Untreated primary		Digested primary		Activated range
	Range	Typical	Range	Typical	
Total dry solids (TS), %	2.0–8.0	5.0	6.0–12.0	10.0	0.83–1.16
Volatile solids (% of TS)	60–80	65	30–60	40	59–88
Grease and fats (% of TS)					
Ether soluble	6–30	—	5–20	18	—
Ether extract	7–35	—	—	—	5–12
Protein (% of TS)	20–30	25	15–20	18	32–41
Nitrogen (N, % of TS)	1.5–4	2.5	1.6–6.0	3.0	2.4–5.0
Phosphorous (P_2O_5, % of TS)	0.8–2.8	1.6	1.5–4.0	2.5	2.8–11.0
Potash (K_2O, % of TS)	0–1	0.4	0.0–3.0	1.0	0.5–0.7
Cellulose (% of TS)	8.0–15.0	10.0	8.0–15.0	10.0	—
Iron (not as sulfide)	2.0–4.0	2.5	3.0–8.0	4.0	—
Silica (SiO_2, % of TS)	15.0–20.0	—	10.0–20.0	—	—
Alkalinity (mg/l as $CaCO_3$)	500–1500	600	2500–3500		580–1100
Organic acids (mg/l as Hac)	200–2000	500	100–600	3000	1100–1700
Energy content	10,000–12,500	11,000	4000–6000	200	8000–10,000
pH	5.0–8.0	6.0	6.5–7.5	7.0	6.5–8.0

Sources: [1].

4. Extractabilities of heavy metals in sludge

Because of the physical–chemical processes that are involved in activated wastewater sludge treatment, sludge tends to accumulate heavy metals existing in the wastewater [9]. Heavy metals such as zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), mercury (Hg) and chromium (Cr) are principal elements restricting the use of sludge for agricultural purposes [9]. Their potential accumulation in human tissues and biomagnifications through the food-chain create both human health and environmental concerns [10]. The mobility of trace metals, their bioavailability and related eco-toxicity to plants, depend strongly on their specific chemical forms or ways of binding [11]. Concentrations of heavy metals in sewage sludge may vary widely, depending on the sludge origins. Typical metal concentrations are indicated in Table 2 [1,9].

Much experimental work is performed worldwide to determine the extractable trace metals in sludge to assess the bio-available metal fraction and the potential mobility of trace metals from polluted sludge. Over the last decades, a great variety of extraction schemes, both simple and sequential have been developed and, although some methods have been widely used [12,13] none has been unreservedly accepted by the scientific community. Characteristically, although there is a wide range of procedures which can be used, their results are not comparable since they present significant variations that depend on the extraction method [14]. Alonso Àlvarez et al. [15] have investigated the sequential extraction of Al, Cd, Co, Cu, Cr, Fe, Mn, Hg, Mo, Ni, Pb, Ti and Zn, from five sludge samples of five different municipal activated sludge plants. The experiments were carried out according to Community Bureau of Reference (BCR)'s scheme. It is obvious that the conclusions of such a work are crucial not only to track the evolution of chemical forms of heavy metals throughout the sludge treatment but also to suggest their potential disposal options. The specific work recorded that, in relation to potential toxic effects, Cd, Co, Mo,

Table 2
Typical metal content in wastewater sludge

Metal	Dry sludge (mg/kg)	
	Range	Median
Arsenic	1.1–230	10
Cadmium	1–3.410	10
Chromium	10–990,000	500
Cobalt	11.3–2490	30
Copper	84–17,000	800
Iron	1000–154,000	17,000
Lead	13–26,000	500
Manganese	32–9870	260
Mercury	0.6–56	6
Molybdenum	0.1–214	4
Nickel	2–5300	80
Selenium	1.7–17.2	5
Tin	2.6–329	14
Zinc	101–49,000	1700

Sources: [1,9].

Ni and Ti are safe because of their low levels, compared to Cr, Cu, and Pb which are in high concentration and their elemental toxicity require a more rigorous study in order to be able to predict any possible harmful effects on the biological processes in sludge treatment or in the reuse or final disposal of these.

Fuentes et al. [11], carried out experimental work on four parallel sludge samples deriving from different wastewater plant treatment and that were subsequently stabilized (or not) in different ways; anaerobically, aerobically, in a waste stabilization pond and one unstabilized. The aim of that work was to establish the influence of the stabilization method on the mobility of the heavy metals associated to each phase. Additionally, concentrations of heavy metals were determined as pseudo-total, diethylenetriamineoentaacetic acid (DTPA)-extractable and water-soluble fraction using mixed acid digestion, DTPA and distilled water, respectively. It should be noted that DTPA extraction provides a chemical evaluation of the amount of metals that are available for plant uptake. The results have shown that all four types could be used for soil amendment, due to their high organic matter content and their content in N, P and K, and since the concentration of heavy metals are not in excess. However, the anaerobic digested sludge should not be used for agricultural purposes, because of its high Cr content. The WSP sludge, which had undergone a higher degree of mineralization and stabilization than the other types of sludge showed a lower metal availability index. The latter is explained by the fact that all heavy metals in WSP sludge were associated to the oxidizable and residual fractions, which are the least mobile. On the contrary, the unstabilized sludge contained the highest accumulations of heavy metals in the most easily assimilable fractions (bio-available, exchangeable and reducible).

Hsiau and Lo [9] investigated the extractabilities of heavy metals in chemically fixed sewage sludge, including lime-treated sludge (CS), lime–sodium silicate-treated sludge (LSS), cement-treated sludge (CS) and cement–sodium silicate-treated sludge (CSS), using sequential extraction and single extraction. As a reference case untreated sludge was also investigated. Sequential extraction revealed that the percentages of the heavy metals of organically bound form and exchangeable form, in all sludge samples were in the order of $Cu > Pb > Cr > Zn$. The results of single extraction, conducted at various pH, suggested that the phenomenon mentioned above was attributed to the irreversible dissolution of the metals (e.g. Cu) having higher affinity to organics at very high pH (10.64–12.05) during processing and air drying (20–25 °C) of these chemically fixed sludge.

5. Sludge treatment and disposal in practice

The various options available for sludge handling are presented in Table 3 [7]. The decision-makers should combine in the optimum way the following alternatives, in relation to sludge handling, bearing in mind all the technical, economical and environmental data.

5.1. Main methods in sludge handling

As discussed above, sludge is generated in primary, secondary and advanced wastewater treatment processes. Accordingly, it is classified in the following categories: primary, secondary and sludge produced in the advanced wastewater treatment. Primary sludge

Table 3
Illustration of different major options for sludge handling

Option	Purpose	Application in sludge handling
No use	Stop use of an unwanted substance due to detrimental and irreversible effects to the environment	Effective control of industrial discharges, use of environmentally friendly consumer products etc to facilitate sludge use in agriculture and use of sludge products
Reuse	Decrease of the amount reaching the environment and of extraction of mineral resources by reusing the compound	Internal reuse of materials (as reuse of precipitation chemicals) and external reuse (as reuse of phosphorous as fertilizer)
Convert	Conversion of a substance from an obnoxious form to a form, acceptable for further transport by air, or water or in solid form	Conversion of organics to methane gas (for further use as energy source), solubilization of sludge components for product recovery, conversion of sludge into compost, etc.
Contain	To contain the residues with as low leaching ability as possible	Separate containment of toxic substances in the sludge, inclusion or stabilization of ashes from sludge incineration, etc.
Disperse	Dispersion into environment without negative impact	Effective dispersion of sludge in agricultural use, effective dispersion of untreated flue gases in sludge incineration

Source: [7].

consists of settable solids carried in the raw wastewater; secondary sludge consists of biological solids as well as additional settable solids. Sludge produced in the advanced wastewater may consist of well-resistant viruses, heavy metals, phosphorous or nitrogen [16].

In a large centralized municipal wastewater treatment plant in Europe, before disposal, municipal sludge has to be treated to eliminate the bacteria, viruses and organic pollutants. A typical process is summarized as follows [1]:

- preliminary treatment (screening, comminuting);
- primary thickening (gravity, flotation, drainage, belt, centrifuges);
- liquid sludge stabilization (anaerobic digestion, aerobic digestion, lime addition);
- secondary thickening (gravity, flotation, drainage, belt, centrifuges);
- conditioning (elutriation, chemical, thermal);
- dewatering (plate press, belt press, centrifuge, drying bed);
- final treatment (composting, drying, line addition, incineration, wet oxidation, pyrolysis, disinfection);
- storage (liquid sludge, dry sludge, compost, ash);
- transportation (road, pipeline, sea);
- final destination (landfill, agriculture/horticulture, forest, reclaimed land, land building, other uses).

Table 4 presents indicative examples of sludge treatment processes [1,17].

Table 4
Examples of effective sludge treatment processes used in Europe currently

Process	Description
Sludge pasteurization	Min. of 20 min at 70 °C or min. of 4 h at 55 °C, followed in all cases by primary mesophilic anaerobic digestion
Mesophilic anaerobic digestion	Mean retention period of at least 12 or 24 days primary digestion in temperature range 35 ± 3 or 25 ± 3 °C, respectively, followed by a stage providing a mean retention period or at least 14 days
Thermophilic aerobic digestion	Mean retention period of at 7 days digestion. All sludge to be subject to a minimum of 55 °C for a period of maturation adequate to ensure that compost reaction process is substantially complete
Composting (windows and aerated piles)	The compost must be maintained at 40 °C at least 5 days and for 4 hours during this period at a minimum of 55 °C within the body of the pile followed by a period of maturation adequate to ensure that the compost reaction process is substantially complete
Lime stabilization of liquid sludge	Addition of lime to raise pH to greater than 12.0 and sufficient to ensure that the pH is not less than 12 for a minimum period of 2 h. The sludge can then be used directly
Liquid storage	Storage of retreated liquid sludge for a minimum period of 3 months
Dewatering and storage	Conditioning of untreated sludge with lime followed by dewatering and storage of the cake for a minimum period of 3 months. Storage for a period of 14 days if sludge has been subject to primary mesophilic anaerobic digestion

Sources: [1,17].

5.2. Disposal strategies for municipal sludge

During the last decades there has been a major change in the ways sludge is disposed. Prior to 1998, municipal sludge was primarily disposed at seawaters or was either used as a fertilizer on agricultural land [18]. An alternative was sludge incineration or simply landfilling. Since 1998 onwards, European legislation (UWWTD) prohibits the sea disposal of sewage sludge, in order to protect the marine environment and so it in parallel sludge deposits in landfills will be phased out (yet 35–45% of the sludge in Europe is still landfilled). It is true to say, the agricultural use has become the principal disposal method for sewage sludge; 37% of the sludge produced is being utilized in agriculture, 11% is being incinerated, 40% is landfilled while 12% is used in some other areas such as forestry, sulviculture, land reclamation, etc. The latest trends in the field of sludge management, i.e. combustion, wet oxidation, pyrolysis, gasification and co-combustion of sewage sludge with other materials for further use as energy source, have generated significant scientific interest.

5.2.1. Agricultural reuse

Sewage sludge contains nitrogen and phosphorous, resulting especially from nitrification–denitrification phases in wastewater treatment process [1]. This gives sludge unique fertilizing benefits, since those elements, contained in sludge, are essential to plants for growing. However, sludge may contain at the same time various other elements, which can

be harmful when entering in human food chain, such as heavy metals. Sludge reuse in agriculture was introduced and implemented by the Directive 86/278/EEC, which principal goal is the soil and human protection from the presence of unwanted substances [5]. The Directive is currently under revision. The alterations which should be made, concern mainly the necessity for treatment in sludge before being used, the establishment of lower limits in metal content as well as the introduction of some new criteria (PAH content).

However, on the contrary the reuse of sewage sludge for agricultural purposes faces social and technical obstacles [3]. Technical problems arise due to the fact that sludge is being produced all year round whereas its application on land takes place once or twice a year; consequently the sludge should be stored. Furthermore, the sludge content in specific substances should meet explicit criteria; however these norms are sometimes very perplexed. Another prohibiting factor of larger quantities of sewage sludge being reused in agriculture is the presence of heavy metals.

In addition, social recognition remains the ‘‘black hole’’ in the picture. The development of sludge recycling, in agriculture, collates, in a grade degree, with the possibilities to improve the quality of sludge itself and make the public confident in the above issue [19]. The fact that the debate on sludge disposal and recycling is constantly increasing across Europe shows that the relationship between farmers and their customers, the food industry and retailers is of vital importance for accepting sludge use in agriculture.

5.2.2. Incineration

Incineration remains as the most attractive disposal method, currently in Europe. One should have in mind that legal limitations concerning landfilling and agricultural reuse as well as that sea disposal is no longer an outlet. In that context he should expect that there will be an increase in the role of incineration in the long term [20]. The technology of incineration in terms of the process engineering, energy efficiency and compactness of plant has experienced great improvement lately. Modern fluidized bed incinerators have become more and more attractive both in terms of capital as well as operating costs, in comparison to the conventional multiple hearth type [21]. The advantages of incineration can be summarized as follows:

- Large reduction of sludge volume; researchers have concluded that the final sludge volume after incineration is approximately 10% of that after mechanical dewatering.
- Thermal destruction of toxic organic compounds [22].
- The calorific value of sewage sludge is almost equal to that of brown coal; therefore incineration offers the possibility of recovering that energy content.
- Minimization of odor generation.

Nevertheless, incineration does not constitute a complete disposal method since approximately 30% of the solids remain as ash [20]. This ash is generally landfilled and in certain cases, it is considered as highly toxic because of its metal content. On of the major constraints in the widespread use of incineration is the public concern about possible harmful emissions. However, introducing new technologies for controlling gaseous emissions can minimize the adverse effects mentioned beforehand, while the reduction in the correspondent cost gives incineration considerable advantages in future as compared to other available disposal routes. The amount of sludge being incinerated in Denmark has already reached the percentage of 24% of the sludge produced, 20% in France, 15% in

Belgium, 14% in Germany while in USA and Japan the percentage has increased to 25% and 55%, respectively [7].

5.3. Restrictions in sludge-handling strategies

According to the principles of sustainability several restrictions must be imposed on the implementation of the disposal routes identified above. Some of those restrictions as to sludge-handling methods, based on sustainability are presented in Table 5 [7].

6. Review of thermal processes

Lately, various modern technologies have been introduced, offering an alternative trend to the sewage sludge disposal, especially with the decreasing availability and the increasing price of land for landfilling. These technologies can be grouped in the category of thermal utilization of sewage sludge; pyrolysis, gasification, wet oxidation, combustion is the main representatives of the above group. Thermal processes involve removing of the organic part of the sludge, leaving only the ash component for final disposal. Sewage sludge is a type of biomass fuel and, as mentioned previously and its calorific value is similar to coal (see Table 6) [1]. The principal goal of thermal processing of sewage sludge is the utilization of the stored energy in sludge and the minimization of environmental impacts at the same time, in order to meet the increasingly stringent standards. It is well known that sludge contains high moisture contents. Therefore the majority of energy released during thermal processes is consumed to reduce the amount of moisture [23]. However these routes are

Table 5
Restrictions on sludge managing based on the principles of sustainability

Sludge handling method	Restrictions based/due to/related
Agricultural use (similar restrictions for horticulture and forests)	• Sludge components (metals, toxic organics, pathogens) • Nutrients and metals supply to land • Acceptance from food industry and public • Technical restrictions (handling of the sludge, etc.)
Land deposition	• Maximum organic contents in the sludge • Costs based on fees • Scarcity of land • Permits of new land fill areas • Recycling requirements (i.e. pathogens)
Land Building and reclamation	• Permits of building an incineration plant • Possibilities of co-incineration • Costs (including costs for treatment of flue gases and ashes)
Product recovery from sludge	• Acceptance from users of the sludge products (market considerations) • Needs of resources for product recovery (chemicals, energy, costs, etc.) • Restrictions due to technical problems

Table 6
Typical heating values for several types of sewage sludge

Type of sludge	Heating value (MJ/Kg of DS)	
	Range	Typical
Raw sludge	23–29	25.5
Activated sludge	16–23	21
Anaerobically digested primary sludge	9–13	11
Raw chemically precipitated primary sludge	14–18	16
Biological filter sludge	16–23	19.5

generally considered to be self-sufficient in energy. The main problem concerning thermal processes includes the following [22]: (a) excessive energy necessary to reach high temperatures; (b) high capital costs; (c) need for extensive air pollution equipment.

Presently, a short report will be attempted to combustion and wet oxidation, while a more extensive review of current literature will be carried out, concerning pyrolysis and gasification.

6.1. Combustion

Over the recent decades, several technologies have been developed in the market for the thermal processing of sewage sludge. Mono- and co-combustion of sewage sludge is perhaps the most established ones, with mono-combustion being even more predominant. Multiple hearth and fluidized bed furnaces are the most popular and the latter is becoming widely applied [24]. The difference between the two types of furnaces is that multiple hearth furnaces usually burn mechanically dewatered (wet) sludge, while fluidized bed furnaces can burn both wet and semi-dried sludge, with dry matter content in the range of 41–65 wt%. Notably, the mechanisms of combustion should be well known, before any prediction of the potential results is made. And this is mainly due to the fact that sludge is expected to exhibit totally different characteristics, when being burnt, from coal. For example sewage sludge has a maximum of 80 wt% moisture content, 50 wt% as (dry mass), 90 wt% volatiles (dry and ash-free mass) and fixed carbon less than 10% [25]. Dominant parameters that may potentially affect the overall combustion process of sewage sludge are the drying of sludge, the release and combustion of the volatiles and the combustion of the high ash content remaining as char. Based on the composition of sewage sludge, presented earlier in Table 1, combustion of sludge may be seen as potential source of various pollutants and care must be taken during its disposal. The following sources of pollutants are important for public health [26]:

- Release of heavy metals.
- The handling of solid residues, e.g. bed and filter ash.
- Emissions of dioxins and furans, NO_x, N_2O, SO_2, as HCl, HF and C_xH_y.

With regard to the combustion of sludge, of greatest concern is the release of gaseous and solid pollutants into the atmosphere. Furthermore, potential problems of ash disposal and leaching of heavy metals may be handled with or restricted with raising temperature

during combustion or even using gasification, the problem of heavy metals still remains unsolved in the conventional multiple and fluidized bed furnaces [26]. As far as the emissions of mercury, dioxins and furans are concerned, these are controllable; characteristically, currently many large scale incinerators of sewage sludge function in such a way that stringent emission limits are met, using state-of art technologies [27]. Despite of the noticeable content of sewage sludge in nitrogen, the conversion ratio of fuel N to NO_x is less than 5%, and the total net emissions of NO_x are in very low levels [28]. From this aspect of view, the raising public concern of potential of adverse effects of sewage sludge combustion is generally unwarranted.

6.2. Wet oxidation

Wet oxidation of sewage sludge is included in the category of thermal processes. It takes place in an aqueous phase at temperatures of 150–330 °C and pressures of 1–22 MPa using pure or atmospheric oxygen. The high temperature is needed to prevent boiling at the temperatures required for the process [8]. During the process, the organic content of sewage sludge is thermally degraded, hydrolyzed, oxidized and converted to carbon dioxide, water and nitrogen. The whole process is occurring in two distinctive regimes [24]:

- The first occurs at sub-critical conditions which occurs below 374 °C and a pressure of 10 MPa.
- The second at supercritical conditions below 374 °C and a pressure of 21.8 MPa.

Data are available in literature providing information relating to the application of the wet-oxidation method on large-scale plants, e.g. at Apeldoorn, The Netherlands [29].

6.3. Pyrolysis

Pyrolysis is the process through which, organic substances are thermally decomposed in an oxygen-free atmosphere, at temperatures varying in the range of 300 and 900 °C. In other words, pyrolysis involves heating of sewage sludge in an inert atmosphere and the consequently release of organic matter and its potential recycling. This technique appears to be less pollutant than conventional methods (incineration, combustion), as it concentrates the heavy metals in a solid carbonaceous residue, so its leaching is not that crucial as that in ashes from incineration [30]. The reactions that take place are thermal cracking and condensation reactions. Compared to combustion process, which is highly exothermic, pyrolysis is rather endothermic, on the order of 100 $KJ\,Kg^{-1}$ [22].

$$\text{Organic} + \text{energy (poor } O_2 \text{ atmosphere)} \rightarrow CH_4 + CO + H_2 + \ldots + \text{energy}.$$

The major fractions that are formed after thermal degradation of the sludge in an inert atmosphere or vacuum are the following [31]:

1. The gaseous fraction; this non-condensable gas (NCG) contains mainly hydrogen, methane, carbon monoxide, carbon dioxide, and several other gases in smaller concentrations.
2. The liquid fraction; this stream consists of a tar and/or oil, which contains substances such as acetic acid, acetone, and methanol.

3. The solid fraction that consists mainly of char, which is most of times pure carbon with small amounts of inert materials.

It should be stated that the proportion of there three phases depends on temperature, reactor residence time, pressure, turbulence, and also the characteristics of the effluent (pH, OM%, DM%). Pyrolysis gas can be used as fuel, as well as the char, while pyrolysis oil can be used as raw material for chemical industries, even as fuel. According to Khiari et al. [22] pyrolysis process can be thoroughly studied using TG, DSC or MS. They distinguished the process into three stages:

1. Vaporization of volatile materials.
2. Primary decomposition of non-volatile components, resulting to solid char. Apart from the char, tar and gases are also produced.
3. The char may undergo secondary higher pyrolysis. In this stage many of the hydrocarbons and aromatic compounds are found in the final volatile phase.

Many researchers have focused on how the different fractions are formed during pyrolysis, using primarily fixed beds, rotary reactors [32]. Also microwave treatment of sewage sludge has shown that when raw wet sewage sludge is treated in the microwave, the only effect that takes place is drying. However, if raw sludge is mixed with microwave receptor like char, which is pyrolysis's product itself, then high temperatures, in the order of 900 °C can be achieved, and pyrolysis occur rather than drying [30]. Moreover in this study it is reported that, compared to conventional heating in electrical furnaces or fluidized bed reactors, microwave treatment saves time and energy for the same level of pyrolysis. Experimental studies in sludge low-temperature pyrolysis in fluidized-bed reactors have come to very interesting conclusions, corresponding with product distribution of sewage sludge after it has undergone pyrolysis treatment [32]. With temperature varying between 300 and 600 °C and gas residence time varying from 1.5 to 3.5 s, three types of products are formed, the NCG, the oil and the car. Shen and Zhang [32] reported that methods that are used to analyze the oil obtained from pyrolysis are usually GC-MS. With this the molecular distribution and structure oil can be investigated. The maximum oil yield (30%) is achieved at the temperature of 525 °C and gas residence time 1.5 s. The oil yield increases with temperature, due to the fact that sludge is subject to more energy, stronger bonds break and thus an increase in larger compounds is observed. Increasing temperature above 525 °C as well as the residence time, oil yield decreases since secondary-cracking reactions occur and so the production of NCG is favored. There is an extensive literature concerning the various temperatures where chemical substances decompose (see Table 7) [33]. From the above table it can be easily drawn, that at 525 °C where the maximum oil yield is achieved, carboxylic and phenolic compounds are decomposed, suggesting that these are the substances of sludge that finally generate the oil. Notably, GC-MS analysis and the following H NMR analysis reveal that the structure of sewage sludge oil consists of a group of aromatic clusters connected by long straight chain hydrocarbons with hydroxyl groups. Literature reports demonstrate that better utilization of sludge oil as fuel is achieved, when straight chain hydrocarbons exist. This is due to the fact that the main characteristics of these types of hydrocarbons are high heating value and low viscosity. It is also stated in these reports that char form sludge pyrolysis affects by a catalytic way to convert the oil from sludge (wide known as OFS) into straight chain

Table 7
Temperature ranges for different substances to decompose

Compounds	Temperature range (°C)
Moisture	Up to 150
Carboxylic	150–600
Phenolic	300–600
Ether oxygen	Up to 600
Cellulosic	Up to 650
Oxygen containing compounds	150–900

Source: [33].

hydrocarbons [34]. Although the exact mechanism of such a process is not completely known a convincing explanation could be the catalytic action of some heavy metals contained in char in the form of salts. Thus if a second reactor is installed to pyrolyze OFS further more, using char as a catalyst, the final product may consist a valuable fuel source. Caballero et al. (1995) [35] claim that thermogravimetric analysis (TGA) is capable of providing pyrolysis kinetic data of sludge at selected temperatures. Other literature reviews on that area, are these of Urban and Antal (1982) [36] who present experimental data on the pyrolysis kinetics of sewage sludge, using TGA. Especially the latter report focuses on the development of a model that could predict the weight loss in a fluidized bed reactor. Working in the same field, Conesa et al. (1997) [37] proposed a kinetic model to describe the pyrolysis of anaerobically digested and non-digested sewage sludge.

Another theme that generates much of interest, mainly because it is lacking in current literature, is the analysis of the thermal pyrolysis characteristics of polymer flocculated waste activated sludge. Polymer flocculation is useful treatments to improve sludge dewater ability [38]. The dosage of flocculent that is sufficient to achieve the best possible sludge dewater ability is generally very low in raw sludge, in the range of ppm. Nonetheless, in dried filtered sludge, flocculent concentration could reach up to 1% by weight! Experiments using TGA on various flocculated sludge samples, obtained from different types of wastewater treatment, have shown that at low heating rate ($\sim 8\,°C\,min^{-1}$) the addition of sludge flocculent (e.g. cationic polyacrylamide) does not affect greatly the pyrolysis rate up to 500–600 °C. In contrary, at high heating rates (~ 14 or $20\,°C\,min^{-1}$) the flocculent markedly enhances the pyrolysis rate.

Piskorz et al. [39] has reported the flash pyrolysis of sewage sludge using a bench scale fluidized bed reactor. During the process the dried mixture of raw and activated sludge was pyrolyzed at reactor residence time less than 1 s over a temperature range of 400–600 °C. Chu et al. [38] investigated in their report the composition of non-condensation gas from wastewater solid pyrolysis. This gas composition was hydrogen, carbon monoxide, carbon dioxide and methane.

6.4. *Gasification*

Technologies which allow utilization of wastes as fuel are of great importance. Theoretically, almost all kinds of organic wastes with moisture content of 5–30% can be gratified; however, not every biofuel can lead to the successful gasification [40]. It was recognized that fuel properties such as surface, size, shape as well as moisture content,

volatile matter and carbon content influence gasification. As the feedstock utilized in gasification, inexpensive materials such as sludge, would be practical. The energy content of the gas produced through gasification depends on numerous factors, such as the feed fuel, reactor type, etc. Therefore, fundamental research regarding the effects of sludge on gasification is important in attempts to obtain a desirable gas for electricity production. Gasification technology can be applied to convert the sewage sludge into a useable energy and to reduce the environmental problem [41,42]. Few studies have been conducted on sewage gasification.

Electricity is an attractive product for its relatively high value, ease of distribution and ease of adapting to local or national market specifications. In addition, the electricity market in Europe offers significant incentives, up to €0.1/kWh, for power generated from renewable resources. Engines and turbines need further development to provide necessary performance guarantees. The main attraction of using gas turbines to convert the energy in biofuel to electricity is the potentially high cycle efficiency. The choice between gas engines and gas turbines is mainly a matter of size (turbines are more appropriate for larger size plants, gas engines for smaller ones).

Gasification is the thermal process during which carbonaceous content of sewage sludge is converted to combustible gas and ash in a net reducing atmosphere. Moreover one could state that the optimum targets of sewage sludge gasification are the production of clean-combustible gas at high efficiency. Compared to incineration, gasification, due to fact that it is a net chemically reductive process, can prevent problems from occurring, including the need for supplemental fuel, emissions of sulfur oxides, nitrogen oxides, heavy metals and fly ash and the potential production of chlorinated dibezodioxins and dibenzofurans [43].

As stated in literature [43], gasification is a series of complex sequential chemical and thermal sub-processes. The total process is actually energetically self-sustaining and usually in steady conditions no energy input is necessary. During the gasification process, sewage sludge undergoes a complex physical and chemical change, starting with the drying or removal of water contained as moisture. The dried sewage sludge is then pyrolysed or thermally decomposed. In the final step, the pyrolysis products, condensable and non-condensable vapors and char undergo gasification, where they are concurrently oxidized and then reduced to permanent gases at the reduction zone. In the drying zone, sewage sludge descends into the gasifier and moisture is evaporated using the heat generated in the zones below. The rate of drying depends on the surface area of the fuel, the recirculation velocity, the relative humidity of these gases and temperature differences between the feed and hot gases as well as internal diffusivity of moisture within the fuel. Characteristically, sludge with less than 15% moisture loses all moisture in this zone [44].

6.4.1. *Gases produced from gasification process*

The actual process is constituted of several repeated cycles of mixing char residue, from previous gasification, with moist sludge, drying and gasification. This results to almost total conversion of all of the organic carbon in sludge to combustible gas and mineral residue [43,45].

Experimental work, using a 5 kWe downdraft gasifier, carried out by Dogru et al. [44], has concluded that the production of clinker in the grate of the gasifier is minor, and in any case easily handled by a better, more suitable design of the grate. Table 8 gives typical

Table 8
Typical combustible gas composition from gasification (vol%)

Gas constituents	vol%
Carbon monoxide, CO	6.28–10.77
Hydrogen, H_2	8.89–11.17
Methane, CH_4	1.26–2.09
C_2H_6	0.15–0.27
C_2H_2	0.62–0.95

concentrations of the combustible gases produced; during the gasification. The quality product gas from sewage sludge was estimated in 4 MJ m^{-3}. This energy content is quite sufficient for internal use. According to Hamiltom [46] the combustible gas produced during gasification, is of high quality that can be utilized for power generation to produce heat for sludge drying. The overall conclusion of Dogru et al. (2002) [44] work is that the small-scale gasifiers can make an important contribution to the economy of rural areas where sewage sludge is abundantly produced.

6.4.2. Fate of heavy metals in gasification

Heavy metals presented in sewage sludge feed-stream are accumulated to the final residue, rendering its disposal problematic. Therefore, it is crucial to ascertain any mobility of heavy metals and where they finally end. Potentially, heavy metals can be met in the following phases of the gasification process: (a) the char residue in the gasifier; (b) the condensate; (c) the char filter. Additionally, it is very important to determine whether there is any metal exit with the gas produced. Marrero et al. [43] have undertaken study to determine the behavior and fates of selected heavy metals during the gasification process—radioactive Cd, cesium (Cs), Co, arsenic (As), Hg, Zn, Cu. As far as the fate of heavy metals is concerned, Reed et al. [47] noted that if no turbulent conditions are achieved, particulate emissions are eliminated to a grate extent. In that case the only major carrier of heavy metals is the fine dust ash. Marrero et al.'s (2003) [43] study has come to the following conclusions:

- Cd, strontium, Cs, Co and Zn are completely retained by the char in the gasifier.
- A very small percentage of Cu is mobilized, most of which is retained in the condensate and the sludge char filter.
- Arsenic is mobilized in a small but significant extent.
- Mercury is the most mobile metal, retained by the char filter.

It should be also stated that during the process, significant amount of aerosols is generated, giving rise to problems of some volatile elements entering into the vapor phase. Arsenic is likely to be one of these elements. Characteristically, the following table contains data concerning the percent of metals retained in the char product of gasification. The measurements were obtained by leaching with 50% nitric acid. As table demonstrates, low retention of metals on the char is achieved and only arsenic presents more than 50% retention.

6.4.3. Hydrogen production from sewage sludge

Almost all of the hydrogen produced today is by steam reforming of natural gas and for the near term, this method of production will continue to dominate. Researchers at are developing a wide range of advanced processes for producing hydrogen economically from sustainable resources. At a time when industrial society is beginning to perceive the end of the period of relatively inexpensive oil, and when the collective consciousness is beginning to change in favor of the fight against the greenhouse effect the use of the biomass and waste as energy sources, and/or the supply of hydrogen, constitutes a particularly attractive alternative and is a major issue for the future. Researchers from UK and Turkey have investigated the hydrogen production potential from sewage sludge, by applying downdraft gasification technique [41,42]. Wet sewage sludge can be assumed as one of the most common feedstock to manufacture hydrogen gas all over the world [44]. As mentioned in the literature, hydrogen can also be produced by thermal gasification of biomass such as forestry by-products, straw, municipal solid waste and sewage sludge [48,49]. The processes involved in producing hydrogen from waste resemble the processes in production from fossil fuel. Under high temperatures, the waste breaks down to gas. The gas consists mainly of H_2, CO and methane (CH_4). Steam is then introduced to reform CH_4 to H_2 and CO. CO is then put through the shift process to attain a higher level of hydrogen. The by-product from this process is CO_2, but CO_2 from biomass is considered "neutral" with respect to greenhouse gas, as it does not increase the CO_2 concentration in the atmosphere. The mixed gas can also be used in fuel cells for electricity production.

Compared to conventional processes for production of electric energy from waste, integrated gasification fuel cell systems are preferable. Electrical efficiency over 30% is possible for these systems. This is not possible using traditional technology [50–52]. *Wet sewage sludge can be assumed as one of the most common feedstock to manufacture hydrogen gas all over the world.*

6.5. Utilization of sewage sludge in cement kiln

6.5.1. Co-combustion of sewage sludge in cement manufacturing

The traditional fuels used in the cement-manufacturing process are gas, oil or coal whilst the alternative ones can be materials like waste oils, plastics, auto residues, waste tires and sewage sludge [53]. In order to use these fuels in a cement factory, the composition of the fuel must be precisely known. The choice as to which fuel will be finally used, is based upon several criteria, i.e. the price and the availability, the energy and ash contents, the moisture and volatiles contents. Table 9 reports alternative fuels for the cement industry, grouped

Table 9
Alternative fuel options for the cement industry

Liquid waste fuels	Tar, chemical wastes, distillation residues, waste solvents, used oils, wax suspensions, petrochemical waste, asphalt slurry, paint waste, oil sludge
Solid waste fuels	Petcoke, paper waste, rubber residues, pulp sludge, used tires, battery cases, plastic residues, wood waste, domestic refuse, rice chaff, refuse derived fuel, nut shells, oil-bearing soils, sewage sludge
Gaseous waste	Landfill gas, pyrolysis gas

Source: [53].

into three categories [53]. Käänte et al. [53] at their work, suggest that as a rule of thumb, the maximal sewage sludge feed rate should not be more than 5% of the clinker production capacity of the cement plant. Consequently, for a 2000 t/day cement kiln, a maximum of 100 t/day dry sludge might be used.

The important restriction of the sludge/coal ratio is the emission of harmful substances with the heavy metals and dust. Their concentrations in the flue gas should meet the environmental regulations. The other factor influencing the co-combustion process is the change of physical and thermal properties of the fuel: heating value, moisture content and ash composition. These influence the thermal output, the amount of air required for combustion, the volume of the flue gases and dust concentration and particle distribution [54].

Primary energy consumption in a typical dry process Portland Cement Plant as found in industrialized countries consists of up to 75% of fossil fuel consumption and up to 25% of electricity consumption. Within the fuel category pyroprocessing requires the most energy, consuming 99% of the fuel energy while electricity is mainly used to operate both raw materials (33%) and clinker (38%) crushing and grinding equipment. Additionally, electricity is needed for pyroprocessing (22%) making it by far the most energy intensive step of the production process [55].

6.5.2. *Utilization of sewage sludge in the cement kiln for mortar production*

The resulting sewage sludge ash (SSA) from incineration can be placed in controlled landfills or used in construction to improve certain properties of building materials [53]. SSA has been used to manufacture bricks, to incorporate into concrete mixtures and as a fine aggregate in mortar. Several works have been carried out in this field. In the light of the results from these works it was concluded that the main objective of using treatment plant sludge as an additional component in a construction material, Portland cement concrete, is possible. The most important physical and mechanical properties of concrete-containing treatment plant sludge were evaluated. Nevertheless, it was first necessary to analyze other characteristics such as the origin of the sludge, the materials used, and the compatibility of the sludge within the cement matrix and the production of specimens. The raw materials for cement production are [53]: Limestone or other source of $CaCO_3$ (approximately 80–85% of input); Clay (approximately 15–29% of input); several other materials (a few of % input) to provide the necessary Si, Fe and Al. The process consists of the following steps:

- blending and grinding of the above-mentioned materials;
- heating in a cement kiln to produce clinker;
- grounding of the clinker;
- addition of further minerals (about 10–20% of the mass);
- production of cement.

The rate of input material to output cement is approximately 1.5 kg for 1 kg, respectively. The loss of mass is the quantity of CO_2 that is emitted to the atmosphere. The energy requirement in fuel is around 3700 MJ per tone of clinker. Currently, in EU the cement production was estimated in 172 million tones in 1995, however it is believed that the demand for cement is undergoing a slow long-term decline, approximately 0.4% per year [53,57].

Monzó et al. [57], conducted thorough studies on the effect of SSA on the workability of cement mortars. SSA was collected from the discharge of a selected fluidized bed incinerator. A nonlinear reduction of workability in mortars containing SSA was observed, however, this reduction becomes less important when SSA content in mortars was increased. They also concluded that the decrease of the mortar workability, when partial substitution of Portland cement by SSA takes place, can be explained by the irregular morphology of SSA particles and the high water absorption on SSA particle surfaces. In other experimental work [57] it is reported that SSA behaves as an active material, producing and increase of compressive strength compared to control mortar, probably due to pozzalonic properties of SSA. It should be noted that high sulfur content of SSA (%SO_3 > 10) seems to have little influence on compressive strength of mortars containing SSA. Moreover, Casanova et al. [58] state that cement degradation processes has been observed when gypsum contaminated aggregates or sulfide-bearing aggregates are used in concrete.

6.5.3. Legislative and environmental issues relating to sludge use in mortars

Currently the EU legislation, corresponding to the utilization of fly ash as additive to construction materials (cement and concrete) is the Council Directive on Construction Products (89/106/EEC) which declares that *only products obtained following the specification of the harmonized standards—defined as the technical specifications adopted by the European Committee for Standardization (CEN)—can bear the EC mark (CE) and enter the free market*. Specifications of the CEN concerning the use of fly ash as construction material are contained in EN 450 [59] and EN 197-1 [60] for concrete and cement, respectively. The latter underlies that "*ash stemming from different processes cannot be used for cements complying with this standard*". Both standards impose limits to the maximum content of the following parameters [56]:

- free lime (causing delayed expansion);
- reactive CaO (hardening accelerator);
- sulfate (affecting setting time and strength development);
- chloride (hardening accelerator, which also induces steel corrosion in concrete);
- loss of ignition (interfering with the action of air-entraining agents-which have the functions of stabilizing air bubbles in the concrete mixtures, with the purpose to increase workability and cohesion of the mix, and to improve the resistance to freeze-thaw cycle).

Moreover, there are some harmful compounds that are harmful and yet not predicted by these standards; alkali (that diminish the late strengths of the cement and increase the danger of cement cracking), MgO (hardening accelerator), phosphates (which extend setting time for the finished cement—at a concentration higher than 0.3% as P_2O_5—and inhibit the formation of cement phases crucial for the final strength) and heavy metals (concentration above 0.1% seem to inhibit the setting of the cement, probably due to the formation of protective layers in the cement grains) [56]. At this point it should be noted that the exclusion of ash from co-firing from the list of the additives to construction material of the EN 450 and EN 197-1 creates severe limitations to the application of processes of combined combustion. Experimental work of Cenni et al. [56] has concluded that ash derived from coal and sewage sludge co-firing contains generally less unburned

carbon, alkali, magnesium oxide, chlorine, and sulfate than coal ash. In contrary, free lime concentrations is higher in mixed ash than in coal. In that specific work, also the leaching of Cd, Cu, Cr, Ni, Pb and Zn was studied, and was concluded that the concentration of these metals in the extracts was below the detection limit and also the concentration of Cu and Zn in the extract from fly ash was found to increase with increasing share of sewage sludge in the fuel mixture. From the environmental point of view, the researchers declared that "*excluding* a priori *the use of ash from co-firing as a suitable additive for construction material could cause an unnecessary burden on the environment*" due to the fact that in this case ash should be disposed of in landfill. However, to overcome the above, modification of current European standards is required in order to include limitations on all elements and compounds that are absent in coal but which might be present in other fuels and are noxious.

6.5.4. Leaching of heavy metals from mortars by using sewage sludge

Experimental work carried out by Valls and Vàzquez [55] consisted in subjecting the mortar samples to a process of accelerated carbonation and subsequently assessing the products of the carbonation by magnetic resonance technique (Si RNM-MAS) and its environmental impact by the NEN-7345 monolithic leaching test. The results showed that the carbonation process affects directly the material's process in a way that carbonation gives rise to an increase in the concentration of Ni, Cu and Zn in the leachates. This is true for three reasons:

- Slight increase in the solubility of the metal compounds through the reduction of the pH in the stabilization system.
- The decomposing of the ettringite hydrate that had zinc incorporated in its crystalline structure.
- The polymerization of the C–S–H-releasing metal cations that were linked to the Si–O groups.

In addition, the amount of barium element leaching is much lower in the carbonated system, due to its lower insolubilization through the formation of $BaCO_3$ and $BaSO_4$, with lower solubilities than the barium hydroxide. Analysis has shown that about 78–98% of Cd, Cr, Cu, Ni, Pb and Zn present in the sewage sludge are retained in the ash, whereas up to 98% of the Hg may be released into the atmosphere with the flue gas [24].

6.5.5. Emissions and especially hg emissions from kilns using or not sewage sludge

The operations that generate emissions at a cement-manufacturing plant are [56]: quarrying, raw material crushing, screening, grinding and milling, raw material loading and unloading to storage including open storage pile, bin, hopper or storage tank, clinker production and combustion of fuels in kiln and clinker cooler, product loading and milling, product loading and unloading to and from storage area, raw material and product conveying system and transfer point and product packaging. Emissions from each separate process listed above can be sub-categorized into process emissions and fugitive emissions. The first can be contained in an enclosure and vented to an add-on control equipment (e.g. emissions from milling and grinding operations vented to a bughouse) while the latter are emissions generated from vehicle traveling within the plant, or emissions from wind erosion, re-entrainment and spillage.

Several countries in EU and worldwide are bounded by Kyoto Protocol to reduce their CO_2 emissions. The cement industry is estimated to contribute 5% of global manmade CO_2 emissions [61]. 50% of these stem from chemical changes of raw material, 40% from fuel combustion and 5% from both electric power and transport. In order to achieve lower CO_2 emissions the following practices could be followed:

- Lower clinker content: 50% of CO_2 emissions occur during the process of producing the intermediate product (i.e. clinker). Reductions could be accomplished by diluting the clinker content and grinding the cement finer.
- Increase fuel efficiency: the wet process consumes nearly twice as much fuel as the precalciner process for each tone of cement. However, changing the process is very expensive, and unlikely to be justified solely by fuel savings.
- Alternative fuels: the use of waste fuels, biofuels or sewage sludge in cement manufacturing, replacing partly or fully the conventional fuels, is an action that should be undergo a thorough study as for its energy efficiency.

The observed increase of the CO_2 concentration in the atmosphere, with its negative effect on the global climate, is predominantly caused by the combustion of fossil fuels. Among these fuels, coal is burnt in power plants and industrial installations in large quantities and with increasing tendency [62]. In cement manufacturing, CO_2 is emitted as a result of both fuel combustion and process-related emissions. Most combustion-related CO_2 emissions result from clinker production, and specifically the fuel used for pyro-processing. Fuel requirements and subsequently CO_2 emissions depend partially on whether a wet process or dry process for clinker making is used, as well as the carbon intensity of the fuel inputs. When waste fuels are used (including sewage sludge) CH_4 and nitrous oxide (N_2O) may also be emitted. These two greenhouse gases are more potent than CO_2; however, due to the extremely high temperatures achieved in the kilns and the high combustion efficiency, these emissions may be minimal [63]. Process-related emissions from cement manufacture are generated through a chemical reaction that converts limestone to CaO and CO_2. The quantity of process-related emissions from cement production are proportional to the lime content of the clinker [64]. Experimental studies have shown that increase of the sludge ratio in the fuel have resulted to increase of nitric oxides and sulfur oxides. Since removal of these components from flue gas needs expensive installations, the ratio of sludge in the fuel must be controlled carefully.

Hg is introduced into the cement-manufacturing process as one of the trace elements in the raw materials and fuels. Depending on their origin, alternative raw materials and fuels may have higher or lower contents of Hg. Sewage sludge normally contains 1–4 mg of Hg per kg of dry matter which exists in various compounds. Due to their low boiling temperature, in the kiln, the Hg compounds are readily vaporized and exist in gas form after combustion [20]. It should be noted though, that Hg the gaseous form of Hg is unstable and often at temperatures above 700 °C the compounds decompose to form elementary Hg, which is not readily soluble. Experiments have shown that Hg reacts mainly with HCl, Cl_2 and O_2, to from chloride compounds. Reactions with SO_2, NO_x, NH_3 and H_2S are insignificant. Therefore, the elementary Hg or the mercury chloride ($HgCl_2$) is the predominant species in the flue gas. Because of the selective reactivity of the elementary Hg with HCl and Cl_2, generally the percentage of the elementary species in Hg emissions in the raw gas after the kiln decreases with an increase in the Cl content of the

sludge. In order to alleviate the problems associated with the CO_2 emission, control methods and processes are under investigation worldwide.

In general, one could report, that Hg content ranges over three orders of magnitude. For limestone and marls, the Hg content ranges from 0.005 to 0.46 ppm, while for clay and shales, from 0.005 to 0.45 ppm. The Hg concentration in raw feed entering the kiln is found to range from 0.01 to >1.0 ppm [64]. Nonetheless, data on Hg speciation is nonexistent. In order sufficient knowledge to be acquired, a research and testing program involving fuels and raw materials, the effect of exhaust gas composition including dust and humidity on mercury speciation, and gas-sampling methodology is recommended.

6.5.6. Modelization-optimization of the process using sludge as alternative fuel

An enormous effort has been made recently in the cement-manufacturing industry to replace the conventional fuels with alternative ones, in order to reduce the energy demands per costs in one hand and meet the environmental requirements in the other.

Käänte et al. (2004) [54] in their study they used a commercial tool (ASPEN PLUS) to evaluate different scenarios of fuel being used in the process. The goal was to optimize process control and alternative fuel consumption, while maintaining product quality. The scope of the using model was to describe the behavior of the kiln process when the fuel is fully or partly replaced by an alternative fuel. The reference case of the model was the use of petcoke as the only primary and secondary fuel, while different other scenarios with alternative fuels, replacing partly the primary or secondary fuel, were assessed. The investigated scenarios referred to *meat and bone meal* (MBM) and *sewage sludge* used as alternative fuels. The calculations have shown that for alternative fuels like MBM and SS the air quantity needed is slightly higher (3–4%). In addition, the need for combustion air is about 2% less than in the reference case, while the energy input is only 20 kcal/kg lower than for the reference case. The quality of the clinker does not worsen due to the combustion of sewage sludge. In terms of emissions, the suspended fine limestone particles are effective in the removal of acidic gaseous pollutants from sludge combustion. The heavy metals from sludge are adsorbed on the particles and returned into the kiln after separation in the E-filter. However, one may expect clogging of the cyclone pre-warmer if the sludge has more than 0.2–0.5% Cl. If sewage sludge is intended to be co-fired in cement works, then lime stabilization may be recommended. It has shown that the ash from lime stabilized and conditioned sludge, normally 0.3–0.5 Kg CaO/Kg dry sludge, has compositions closer to those of cements.

7. Conclusions

This paper has sought to review present and future directions of sewage sludge in European Union, considering all the challenges of wastewater management globally. To date most of the sewage sludge produced during municipal effluent treatment has been used in agriculture or disposed off in landfills, or via incineration. However, there are several factors restricting these options, such as the accumulation of undesirable substances to sludge (e.g., heavy metals, pathogens and organic pollutants) which potentially passes to food-chain. Therefore agricultural use is increasingly regarded as an insecure handling route. The other conventional route, sludge disposal in landfills is eliminating due to EU recent legislation and increased costs. Incineration on the other hand provides a large volume reduction of sewage sludge and results in improved thermal

efficiency. However, the scrubbing costs of the product gases for air pollution control are usually very high. The alternative technologies e.g. pyrolysis, wet oxidation, gasification and combined processes have definite advantages over combustion in terms of the cost of flue gas and ash treatment. There are several driving forces for the search of alternative technologies to sewage sludge disposal, the most significant among them are the large quantity of flue gas and ash formed during sewage sludge incineration and the emissions of dioxins, furans, mercury and other heavy metals, NO_x, N_2O and CO.

However, these technologies are just being introduced into the market and thus are not yet as well as tested as perhaps combustion or incineration. All the above issues summed indicate the importance of investigating thoroughly these novel trends in sewage sludge handling.

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